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WATER PESTICIDES NUMBER 3

Bernard J. Moorman, et al

Environmental Control Administration
Cincinnati, Ohio

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WATER PESTICIDES NO. 3

REPORT NUMBER 38

Report of a Study Conducted by
ANALYTICAL REFERENCE SERVICE

Bernard J. Moorman and Earl F. McFarren
Division of Criteria and Standards
Bureau of Water Hygiene

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Environmental Health Service
Cincinnati, Ohio 45213
1970

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I

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II

FOREWORD

The Analytical Reference Service (ARS) is conducted by the Bureau of Water Hygiene of the Environmental Control Administration to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

> Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.
>
> Exchange of information regarding method characteristics.
>
> Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new pollution compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the membership, consultants, and the ARS staff. Notice of each study is sent to the entire membership. To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Now primarily directed toward examination of water, in the past studies have included methods for analysis of air, milk, and food. Some studies are periodically repeated for the advantage of new members, the evaluation of new methods, or the reevaluation of existing methods.

The selection of studies is guided by requests from standard methods committees and the responses to questionnaires periodically circulated among the membership, which now includes 299 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

COMPLETED STUDIES

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium; study No. 1 completed in 1956, No. 2 in 1958 and No. 3 in 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc; study No. 1 completed in 1957 and No. 2 in 1962. These same metals plus silver; study No. 3 completed in 1965. Except for the substitution of magnesium for aluminum, these same metals were analyzed by atomic absorption in 1967; study No. 4. Copper, manganese, and aluminum in the presence and absence of interferences; study No. 5 completed in 1969. Aluminum, beryllium and barium by atomic absorption; study No. 6 completed in 1970.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure; study No. 1 completed in 1958 and No. 2 in 1961. Fluoride by ion-exchange and fluoride electrode; study No. 3 completed in 1969.
Water-Radioactivity	Gross beta activity; study No. 1 completed in 1959 and No. 2 in 1961. Gross beta and strontium-90 activity; study No. 3 completed in 1963.
Water-Surfactant	Surfactant in various waters; study No. 1 completed in 1959, No. 2 in 1963 and No. 3 in 1968.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand; study No. 1 completed in 1960. Chemical oxygen demand; study No. 2 completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium; study No. 1 completed in 1962. These same metals plus vanadium; study No. 2 completed in 1966.

Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification; study No. 1 completed in 1964.
Water-Nutrients	Silicate, phosphate, ammonia nitrogen, organic nitrogen, and nitrate nitrogen; study No. 1 completed in 1966. Ammonia nitrogen, nitrate nitrogen and ortho, poly, and organic phosphate; study No. 2 completed in 1970.
Water-Phenols	Phenol and 2,4-dichlorophenol in water by two specified methods; study No. 1 completed in 1966.
Water-Cyanides	Potassium cyanide and potassium ferricyanide in water by two specified methods; study No. 1 completed in 1967.
Water-chlorine	Free and combined chlorine by nine different methods; study No. 1 completed in 1969.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber, high-volume filter mats; study No. 1 completed in 1958.
Air-Lead	Filter paper tape impregnated with lead; study No. 1 completed in 1961.
Air-Particulates	Microscopic identification of some common atmospheric particulates; study No. 1 completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method; study No. 1 completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water; study No. 1 completed in 1965. Lindane, heptachlor, aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, endrin, o,p'-DDT, p,p'-DDT, and methoxychlor in water; study No. 2 completed in 1968. Lindane, heptachlor epoxide, dieldrin, heptachlor, p,p'-DDT, and endrin; study No. 3 completed in 1970.

Food-Pesticides	DDT in milk; study No. 1 completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in milk; study No. 2 completed in 1965.

Copies of these reports are available from ARS on request as long as the present supply lasts. In most cases reports published prior to 1965 are no longer available. Order by title; namely, Water-Metals No. 4, or Water-Surfactant No. 3, etc.

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PREFACE

The results obtained in a previous study were not as good as desired, perhaps for several reasons; (1) the method as written was not satisfactory if a concentric tube type of electron capture detector was used rather than a parallel plate type, (2) the levels contained in the samples were near the lower limits of sensitivity of the method, and (3) many of the participants failed in analyzing the samples, to follow exactly the prescribed procedure.

In an effort to correct some of these problems the method was entirely rewritten so as to permit the use of either type of detector and the extraction procedure was revised in an effort to improve the sensitivity. However, as a result of some recently proposed pesticide standards for drinking water, it appeared that there was no need for a method which would detect such low levels. Therefore, the concentrations of the pesticides in two of the samples used for this study were increased from ten to fifty fold over those contained in the previous study samples in order to obtain data on the precision and accuracy of the method over a wide range and at or near the level of the proposed drinking water standards.

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ACKNOWLEDGMENT

Dr. A. E. Greenburg, Chief, Sanitation and Radiation Laboratory, State of California, Department of Public Health, assisted in writing, testing and revising the method studied in this collaborative study.

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ABSTRACT

In this study the participants were asked to analyze three samples each of which contained the pesticides lindane, heptachlor, heptachlor epoxide, dieldrin, p,p'-DDT, and endrin but at different concentrations. Each analyst was requested to analyze the samples by a prescribed method, which specified techniques for the extraction and clean-up and suggested the parameters at which to operate the gas chromatograph in the determinative step of the analysis. Each also was requested to provide a chromatogram of a heptachlor standard for use in calculating his column efficiency.

In general, it can be said that no two participants followed exactly the same procedure as ten different gas chromatographs equipped with four different kinds of detectors and twenty-seven different kinds of columns were used. Overall, the accuracy of the data was acceptable, namely, the relative error was over 15 percent in only four cases out of eighteen. On the other hand the precision was unacceptable, namely; in only one case was the relative standard deviation less than 20 percent.

No correlation was found to exist between column efficiency and precision or accuracy obtained.

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WATER PESTICIDES NO. 3

DESIGN OF THE STUDY

For economy, ease in handling and solution stability the samples were sent in 25 ml glass ampoules as concentrated solutions. The pesticides were dissolved in ethyl acetate to permit better dissolution of the sample in distilled water.

After diluting the concentrate with distilled water as prescribed in the instruction sheet (namely, 1 ml to a liter or 5 ml to 5 liters as required to obtain a sufficient size sample) the water samples should have contained the amounts of pesticides indicated in Table 1.

Table 1. COMPOSITION OF SAMPLES

PESTICIDE	Sample 1 µg/liter	Sample 2 µg/liter	Sample 3 µg/liter
Lindane	25.00	5.00	0.50
Heptachlor	15.00	7.50	1.00
Heptachlor Epoxide	15.00	7.50	1.00
Dieldrin	15.00	5.00	0.25
p, p'-DDT	20.00	5.00	0.50
Endrin	10.00	1.00	0.10

The participants were further instructed to analyze each sample for each of the pesticides by the recommended procedure (Appendix A), and to provide a copy of a chromatogram of a heptachlor standard for use in calculating the column efficiency. As indicated in Table 1, each sample contained the same six pesticides which were specified. However, the concentrations of the pesticides varied in each sample. The amounts in sample 1 were about two times that in Sample 2 and the amounts in Sample 2 were about ten times that in Sample 3.

TREATMENT OF THE DATA

As the results from each participant were received the efficiencies of the gas chromatographic columns were calculated (see Appendix C), using the response of the pesticide heptachlor. These values were then listed in ascending order of column efficiency and identified by laboratory number.

For lindane, heptachlor epoxide and p,p'-DDT (early, middle and late eluters, respectively) the deviations of the determined values from the true value were calculated. These too were identified by laboratory number and arrayed in the order of their column efficiencies. Then, for each pesticide, histograms of the deviations versus laboratory number were constructed. Finally, to determine any relationship to the accuracy of the analyses, a plot of column efficiency versus the laboratory number was superimposed over the histogram.

The data also were grouped according to the type of detector and diameter of gas chromatographic column used, which for the most part was dictated by the instrument used. These groups are listed and identified in Table 2. However, only the data obtained with instruments 1, 2 and 3 were statistically evaluated for too few results were available to make possible a comparison of any of the other instruments. All of the results, however, are included under the heading "Overall" in the "Summary of Results" table for each pesticide. Both the overall and the individual groups of data were plotted on probability paper to determine their normality of distribution. Participants whose data were judged not normal were asked to review it to account for and, if possible, correct any error. If the error was indeterminate and the value of the data was 3 sigma beyond the mean, the deviation was considered significant, and therefore was rejected. The accuracy and precision of the remaining results were then calculated, and tested for statistically significant differences among the groups. The accuracies were compared using the test for "Comparing the Averages of Several Products (1)", and the precisions were compared using the "F" test. (See Appendix F).

DISCUSSION OF THE RESULTS

COLUMN EFFICIENCY VERSUS ACCURACY

The histogram showing the deviation of the results from the true value over which was superimposed a plot of values for the column efficiencies, did not demonstrate any relationship. That is to say, the error and efficiency values did not mutually decrease or increase as might be expected.

Table 2. TYPE OF DETECTORS AND SIZE OF COLUMNS USED

Instrumental Method	Description
1. Micro Tek-H^3	130-mc tritium parallel plate electron capture detector with a 1/4" O. D. column.
2. Micro Tek-Ni^{63}	60-mc Ni^{63} parallel plate electron capture detector with a 1/4" O. D. column.
3. Aerograph-H^3	250-mc tritium concentric tube electron capture detector with a 1/8" O. D. column.
4. Barber-Coleman-H^3	250-mc tritium parallel plate electron capture detector with a 1/4" O. D. column.
5. F & M-H^3	200-mc tritium parallel plate electron capture detector with a 1/4" O. D. column.
6. Jarrell-Ash-H^3	200-mc tritium parallel plate electron capture detector (pulsed voltage type) with a 1/4" O. D. column.
7. Beckman-HG	Helium glow discharge (non-radioactive) electron capture detector with a 1/4" O. D. column.
8. Shimadzu-TC	Filament type thermal conductivity detector.
9. Aerograph-MC	Microcoulometric detector with a 1/4" O. D. column.

Listed in Table 3 are the column efficiencies for the various column packings used by the study's participants. These values are based on the responses of heptachlor. As can be noted, the column packings were made up of many concentrations of various liquid phases or combinations of these on several different supports. However, column efficiency is dependent not only on the type and particle size of the support material and the type and percentage of liquid phase loading, but also upon preparation technique, column packing technique, and upon column operating parameters, particularly carrier flow rate (2). Thus, in view of the many variables, it is not surprising that there was no correlation.

Table 3. COLUMN EFFICIENCIES VERSUS COLUMN PACKING

LAB. NO.	Column Efficiency	Column Packing	LAB. NO.	Column Efficiency	Column Packing
3411	0.0622	4% SE-30, 6% QF-1	7622	0.1786	4% DC-200, 6% QF-1
4515	0.0646	3% SE-30	9613	0.1786	11% OV-17, QF-1
8322	0.0651	5% DC-200	1524	0.1793	11% OV-17, QF-1
3511	0.0794	10% DC-200 (Chromoport WHP)	4511	0.1823	10% DC-200
7424	0.0863	3% OV-1	1124	0.1866	11% OV-17, QF-1
6911	0.0875	4% SE-30, 6% QF-1; 1.5% OV-17, 1.95% QF-1	3351	0.1905	QF-1, OV-17 (Gas Chrom Q)
			3611	0.2032	DC-200, QF-1 (ABS)
9111	0.0905	3% DC-200	7813	0.2209	2.4% QF-1, 2.0% SE-30, 0.5% Carbowax 20M
3111	0.0943	1.5% OV-17, 1.95% QF-1			
8211	0.1016	3% DC-200	6552	0.2117	1 pt 5% QF-1, 2 pts 5% Dow 11
6715	0.10409	10% DC-200	9613	0.2333	10% DC-200 (Gas Chrom Q)
4511	0.1055	10% QF-1, 10% DC-200	7914	0.2333	10% DC-200 (Aeropak 30)
4515	0.1191	3% DC-200, 4.5% QF-1	3611	0.241	DC-200 (ABS)
7123	0.1196	DC-200 (Gas Chrom Q)	9111	0.2814	2% QF-1, 3% DC-200
3411	0.1203	1.5% OV-17, 1.95% QF-1	9123	0.304	0.3% DC-200 (Glass Beads)
4611	0.1219	10% DC-200 (Chromoport, 80-90)	0003	0.3106	10% DC-200
8322	0.1236	5% QF-1	5351	0.3175	2% QF-1, 3% DC-200
7112	0.1244	Dow 11 (Chromosorb W)	9123	0.323	2% QF-1
4112	0.1325	10% DC-200	1524	0.3387	10% DC-200 (ABS)
7813	0.1337	5% DC-200, 0.5% Carbowax 20M	2811	0.373	10% DC-200 (Gas Chrom Q)
7911	0.1355	5% OV-1	4611	0.3908	5% DC-200, 15% QF-1
6715	0.1380	11% OV-17, QF-1	5136	0.3942	5% OV-1
1124	0.1407	5% QF-1	4811	0.4572	5% SE-30
3111	0.1475	4% SE-30, 6% QF-1	0003	0.4615	4% DC-200, 6% QF-1
7813	0.1555	5% DC-200	2513	0.5181	8% QF-1, OV-17
7622	0.1578	10% DC-200			
7123	0.1595	QF-1 (Gas Chrom Q)			
7424	0.172	10% DC- 30			
8211	0.1786	3% QF-1			

LINDANE (Tables 4, 5 and 6)

A statistical evaluation of the lindane data from the analysis of samples 1, 2 and 3 (true values: 25.00 µg/1, 5.00 µg/1 and 0.50 µg/1, respectively) by instruments 1, 2 and 3 showed a range for the relative errors from 1.6 percent (instrument 2, sample 3) to 30.4 percent (instrument 1, sample 3) and a range for the relative standard deviations from 14.1 percent (instrument 2, sample 2) to 50.8 percent (instrument 1, sample 2). Except for the 1.6 percent accuracy the data has fair to poor accuracy and in most cases fair to very poor precision.

There are few significant differences among the accuracies of the data obtained by the three instruments. The exceptions are in the data for lindane (0.50 µg/1) in sample 3. Here there are significant differences, apparently due to the instrument used. Data obtained by instrument 2 has the best accuracy (1.6 percent relative error), and instrument 3 (7.3 percent relative error) gave more accurate results than instrument 1 (30.4 percent relative error).

There are even fewer differences in precision. The data for sample 2 by instrument 2 (relative standard deviation 14.1 percent) is significantly more precise thant the data determined by instrument 1 (relative standard deviation 50.8 percent). Comparisons by "F" test of the other variances indicates no other significant differences in precision. A possible reason for the poor lindane results is that the electron capture detector is highly sensitive to lindane. Its chemistry with six chlorine atoms and an unsymetrical configuration gives the molecule strong electronegativity properties. It is this electronegativity that accounts for the high electron affinity of the substance. Because of it the standard curve used in lindane's quantitation has a steep slope to the linear portion. This as a result narrows the range of quantities covered by the linear portion, and also causes the range to extend over quantities that are very small in value. So, to accurately quantitate a lindane sample, it is important to inject a small quantity of the pesticide to obtain a response within the tight limits of the linear portion of the curve. If too large a quantity is injected its response will fall above in the plateau region. Here the slightest variation in measurement will greatly magnify the error.

A second very possible cause of error is the concentration of large volumes of solvents used in the extraction of the pesticides from the sample media and in the clean-up of the extract (3). Contaminants in the solvent may cause great difficulty.

During the processing and analysis some sample solutions are concentrated and reconcentrated several times. Although the solvents used are highly volatile compared to most pesticides, care must be

taken to avoid losses of pesticide during evaporation. Particular care should be used in evaporating solvents containing pesticides with low gas chromatographic retention times; such as lindane, since this is an indication of volatility of the pesticide.

Table 4. SUMMARY OF RESULTS FOR LINDANE IN SAMPLE 1

(25.00 μg/liter)				
Instrument	Micro Tek-H[3]	Micro Tek-Ni[63]	Aero-graph-H[3]	Overall
Number of results	5	6	10	29
Number of outliers	1	2	0	8
Mean	17.32	23.28	21.80	21.87
Mean Error	-7.18	-1.72	-3.20	-3.13
Standard Deviation	5.56	3.39	6.26	5.18
Relative Error	28.7	6.9	12.8	12.5
Relative Standard Deviation	31.2	14.6	28.7	23.7

Table 5. SUMMARY OF RESULTS FOR LINDANE IN SAMPLE 2

(5.00 μg/liter)				
Instrument	Micro Tek-H[3]	Micro Tek-Ni[63]	Aero-graph-H[3]	Overall
Number of results	5	6	9	38
Number of outliers	1	3	1	0
Mean	3.86	4.70	4.53	4.34
Mean Error	-1.14	-0.30	-0.47	-0.66
Standard Deviation	1.96	0.66	1.17	1.85
Relative Error	22.8	6.1	9.3	13.2
Relative Standard Deviation	50.8	14.1	25.8	42.6

Table 6. SUMMARY OF RESULTS FOR LINDANE IN SAMPLE 3

(0.50 μg/liter)				
Instrument	Micro Tek-H[3]	Micro Tek-Ni[63]	Aero-graph-H[3]	Overall
Number of results	6	9	9	36
Number of outliers	0	0	1	0
Mean	0.348	0.508	0.463	0.449
Mean Error	-0.152	0.008	-0.037	-0.051
Standard Deviation	0.108	0.179	0.147	0.155
Relative Error	30.4	1.6	7.3	10.2
Relative Standard Deviation	31.1	35.2	31.8	36.6

HEPTACHLOR (Tables 7, 8 and 9)

The overall data for each concentration of heptachlor has poor accuracy and very poor precision. The data obtained in the analysis of all three samples for heptachlor by the use of instrument 3 has good accuracy, but only fair precision. Data obtained for the three samples using both instruments 1 and 2 have poor accuracy and even poorer precision.

Using the "F" test for comparing variances and the test for "Comparing the Averages of Several Products", some differences among the precisions and accuracies were observed. For heptachlor in sample 3 (1 μg/liter) the data obtained with instrument 3 is significantly more accurate than that obtained with instrument 2, and the data obtained by the use of instrument 1 is the least accurate of the three. Furthermore, it is of interest to note that the relative errors of the data obtained with instruments 1, 2 and 3 on analysis of sample 1 (relative errors of 24.6, 13.0, and 4.9 percent respectively) are similar to those obtained in the analysis of sample 3 (relative errors of 30.5, 8.2, and 3.1 percent respectively). However, no statistically significant differences in the data obtained by any of the instruments in the analysis of sample 1 (15.00 μg/liter) was apparent.

The "F" test indicated that instrument 3 gave more precise results than instrument 1 in analyzing for heptachlor in sample 1 (15.00 μg/liter). Instrument 3 also gave more precise results than both instruments 1 and 2 in analyzing for heptachlor in sample 2 (7.50 μg/liter).

The overall poor results might be attributed to the common error; the improper use of a standard curve. Heptachlor gives a good response in the electron capture detector and like lindane, but to a lesser degree, has a very steep slope in the linear portion of the curve which does not cover a very large range. Thus, the response of too large a quantity will not be within the linear portion of the curve and a large error may result.

Table 7. SUMMARY OF RESULTS FOR HEPTACHLOR IN SAMPLE 1

(15.00 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	6	6	9	34
Number of outliers	0	2	1	3
Mean	11.30	13.05	15.74	12.79
Mean Error	-3.69	-1.95	0.74	-2.21
Standard Deviation	5.19	2.55	2.24	4.13
Relative Error	24.6	13.0	4.9	14.7
Relative Standard Deviation	45.9	19.5	14.2	32.3

Table 8. SUMMARY OF RESULTS FOR HEPTACHLOR IN SAMPLE 2

(7.50 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	6	9	8	36
Number of outliers	0	0	2	2
Mean	5.64	6.37	6.64	6.04
Mean Error	-1.86	-1.13	-0.86	-1.46
Standard Deviation	3.29	2.10	0.95	2.53
Relative Error	24.8	15.0	11.5	19.5
Relative Standard Deviation	58.4	32.9	14.4	41.8

Table 9. SUMMARY OF RESULTS FOR HEPTACHLOR IN SAMPLE 3

(1.00 μg/liter)				
Instrument	Micro Tek-II[3]	Micro Tek-Ni[63]	Aero-graph-II[3]	Overall
Number of results	6	9	8	36
Number of outliers	0	0	2	2
Mean	0.695	0.918	1.031	0.837
Mean Error	-0.305	-0.082	0.031	-0.163
Standard Deviation	0.286	2.35	0.152	0.563
Relative Error	30.5	8.2	3.1	16.3
Relative Standard Deviation	41.1	25.5	14.7	67.3

HEPTACHLOR EPOXIDE (Tables 10, 11 and 12)

The overall heptachlor epoxide data is more accurate and more precise than the overall lindane and heptachlor data. The overall accuracy is 2.5 percent for the analysis of sample 1 (15.00 μg/liter), 1.1 percent for sample 2 (7.50 μg/liter), and 7.0 percent for sample 3 (1.00 μg/liter). The overall precisions for the three samples are respectively 25.4, 22.7, and 20.6 percent. Although better than the overall precision of lindane and heptachlor, the precision is still only fair.

Both instruments 2 and 3 gave good accuracy in the analysis of all three samples (relative errors ranging from 0.4 to 8.8 percent). Although not as good, the results obtained with instrument 1 are not significantly different (relative errors from 8.6 to 15.5 percent).

All the precisions obtained are fair (relative standard deviations ranging from 7.9 to 18.1 percent) except for one poor result obtained by each of the instruments on different samples (relative standard deviations of 22.8, 26.4, and 31.9 percent). The precision obtained by the use of instrument 1 in analyzing sample 2 is significantly better than all of the rest (relative standard deviation of 7.9 percent).

Table 10. SUMMARY OF RESULTS FOR HEPTACHLOR EPOXIDE IN SAMPLE 1

(15.00 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	6	6	10	36
Number of outliers	0	2	0	1
Mean	13.2	13.7	15.4	14.6
Mean Error	-1.83	-1.32	0.44	-0.37
Standard Deviation	3.48	2.46	2.79	3.72
Relative Error	12.2	8.8	2.9	2.5
Relative Standard Deviation	26.4	18.0	18.1	25.4

Table 11. SUMMARY OF RESULTS FOR HEPTACHLOR EPOXIDE IN SAMPLE 2

(7.50 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	4	7	10	35
Number of outliers	2	2	0	3
Mean	6.86	7.53	7.06	7.42
Mean Error	-0.64	0.03	-0.44	-0.08
Standard Deviation	0.54	1.32	1.61	1.69
Relative Error	8.6	0.4	5.9	1.1
Relative Standard Deviation	7.9	17.6	22.8	22.7

Table 12. SUMMARY OF RESULTS FOR HEPTACHLOR EPOXIDE IN SAMPLE 3

(1.00 μg/liter)				
Instrument	Micro Tek-H[3]	Micro Tek-Ni[63]	Aero-graph-H[3]	Overall
Number of results	6	9	8	33
Number of outliers	0	0	2	5
Mean	0.845	0.913	0.984	0.930
Mean Error	-0.155	-0.087	-0.016	-0.070
Standard Deviation	0.153	0.291	0.167	0.192
Relative Error	15.5	8.7	1.6	7.0
Relative Standard Deviation	18.1	31.9	17.0	20.6

DIELDRIN (Tables 13, 14 and 15)

The overall accuracy in the determination of dieldrin in all three samples is fair but the precision is fair only in sample 1 and poor in the other two.

All three instruments gave good accuracy in the analysis of the three samples but the precisions were only fair to poor except for the data obtained by instrument 3 in analyzing sample 1 (relative standard deviation 8.6 percent). In fact, the data obtained with instrument 3 in all three samples is significantly more precise than any of the data obtained by instrument 1.

The analysis of sample 3 (0.25 μg/liter) by instrument 2 gave significantly more accurate results than instruments 1 and 3. However, there is no difference in accuracy between instruments 1 and 3.

Table 13. SUMMARY OF RESULTS FOR DIELDRIN IN SAMPLE 1

(15.00 μg/liter)				
Instrument	Micro Tek-H^{3}	Micro Tek-Ni^{63}	Aero-graph-H^{3}	Overall
Number of results	6	5	7	29
Number of outliers	0	3	3	8
Mean	12.51	12.80	14.53	13.37
Mean Error	-2.49	-2.20	-0.47	-1.63
Standard Deviation	2.61	2.37	1.25	2.70
Relative Error	16.6	14.7	3.1	10.9
Relative Standard Deviation	20.8	18.5	8.6	20.2

Table 14. SUMMARY OF RESULTS FOR DIELDRIN IN SAMPLE 2

(5.00 μg/liter)				
Instrument	Micro Tek-H^{3}	Micro Tek-Ni^{63}	Aero-graph-H^{3}	Overall
Number of results	6	6	9	37
Number of outliers	0	3	1	1
Mean	4.84	4.66	5.02	4.64
Mean Error	-0.16	-0.34	0.02	-0.36
Standard Deviation	1.87	1.00	0.87	1.96
Relative Error	3.2	6.8	0.4	7.2
Relative Standard Deviation	38.6	21.4	17.3	42.2

Table 15. SUMMARY OF RESULTS FOR DIELDRIN IN SAMPLE 3

(0.25 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	6	8	9	32
Number of outliers	0	1	1	6
Mean	0.285	0.236	0.213	0.215
Mean Error	0.035	-0.014	-0.037	-0.035
Standard Deviation	0.230	0.125	0.083	0.077
Relative Error	14.0	5.5	14.8	14.0
Relative Standard Deviation	80.5	52.8	38.9	35.7

p,p'-DDT (Tables 16, 17 and 18)

The overall data and the data obtained by the three instruments indicate good accuracy but only fair precision. In fact, the accuracies and precisions obtained for p,p'-DDT are generally more acceptable than are the data for the other pesticides, but there are some exceptions. The data obtained by instrument 1 in analyzing samples 2 and 3 gave very poor precision (relative standard deviations of 40.1 and 51.1 percent respectively). On the other hand, the accuracy was good, as indicated by relative errors ranging only from 1.0 to 13.8 percent.

The better results obtained for p,p'-DDT might be explained by the fact that the electron capture detector's response to this pesticide results in a curve with less slope and a greater range of linearity. A helpful fact to remember in interpreting the p,p'-DDT chromatogram is the on column conversion of p,p'-DDT to p,p'-DDE or p,p'-DDD. The degree of conversion to DDD (4) depends on the liquid phase, its concentration on the support material and upon the age and history of the column. These degradation products may cause confusion and interference.

Only for sample 3 (0.25 μg/liter) are there significant differences in accuracy among the instruments used. Instrument 1 is more accurate than 2 or 3 and instrument 3 is more accurate than 2.

A comparison of precisions of the three instruments showed that instrument 2 was more precise than instrument 1 in the analysis of each sample. It also demonstrated that instrument 3 was more precise than instrument 1 in the analysis of samples 2 and 3, but that there was no significant difference between instruments 2 and 3.

Table 16. SUMMARY OF RESULTS FOR p, p'-DDT IN SAMPLE 1

(20.00 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	6	6	8	32
Number of outliers	0	2	2	6
Mean	19.46	21.27	20.19	19.47
Mean Error	-0.54	1.27	0.19	-0.53
Standard Deviation	5.05	1.81	3.65	4.81
Relative Error	2.7	6.4	1.0	2.6
Relative Standard Deviation	26.0	8.5	18.0	24.7

Table 17. SUMMARY OF RESULTS FOR p, p'-DDT IN SAMPLE 2

(5.00 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	6	6	10	31
Number of outliers	0	3	0	7
Mean	5.36	5.69	5.39	4.89
Mean Error	0.36	0.69	0.39	-0.11
Standard Deviation	2.15	0.80	0.50	1.17
Relative Error	7.2	13.8	7.8	2.2
Relative Standard Deviation	40.1	14.0	9.2	24.0

Table 18. SUMMARY OF RESULTS FOR p, p'-DDT IN SAMPLE 3

(0.50 μg/liter)				
Instrument	Micro Tek-H[3]	Micro Tek-Ni[63]	Aero-graph-H[3]	Overall
Number of results	6	9	8	36
Number of outliers	0	0	2	2
Mean	0.512	0.550	0.460	0.473
Mean Error	0.012	0.050	-0.040	-0.028
Standard Deviation	0.262	0.118	0.075	0.180
Relative Error	2.4	10.0	8.0	5.6
Relative Standard Deviation	51.1	21.5	16.39	38.2

ENDRIN (Tables 19, 20 and 21)

The accuracies and precisions obtained for the three concentrations of endrin (10.00 μg/liter, 1.00 μg/liter and 0.10 μg/liter) in samples 1, 2, and 3 are the most inconsistent. There are some very good accuracies (0.0 percent relative error for sample 3 by instrument 1) and precisions (5.9 percent relative standard deviation for sample 2 by instrument 1), and some poor accuracies (25.0 and 39.0 percent) and precisions (79.3 and 33.6 percent).

Endrin analysis by gas chromatography may present several rather unique difficulties. It is a late eluter from the chromatographic column which causes a broad peak with little height. Consequently, a plot of response versus increasing quantities of an endrin standard produces a long straight and often nearly horizontal line. As a result, the slightest error in measuring and comparing a response of an unknown endrin sample may be greatly magnified.

Endrin also may undergo complete thermal isomerization on the chromatographic column during analysis to give two substances. A known product (5) of thermal or acid catalyzed rearrangement and an isomeric aldehyde. A dual response results which may cause confusion as well as interference in an analysis.

A comparison of the accuracies of the data obtained shows instrument 3 to be more inaccurate than both instrument 2 and instrument 1 in analyzing for the 1.0 μg of endrin per liter in sample 2. In

analyzing sample 3 (0.10 μg/liter) instrument 1 is more accurate than instruments 2 and 3.

The "F" test shows no differences in precision among the instruments in analyzing sample 1. However, for sample 2, instrument 1 is more precise than instrument 2 or instrument 3. In the analysis of sample 3, instruments 1 and 2 were more precise than instrument 3.

Table 19. SUMMARY OF RESULTS FOR ENDRIN IN SAMPLE 1

(10.00 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	5	7	8	31
Number of outliers	1	1	1	6
Mean	9.39	11.16	11.20	10.85
Mean Error	0.61	1.16	1.20	0.85
Standard Deviation	0.81	1.72	1.55	1.83
Relative Error	6.1	11.6	12.0	8.5
Relative Standard Deviation	8.6	15.4	13.8	16.9

Table 20. SUMMARY OF RESULTS FOR ENDRIN IN SAMPLE 2

(1.00 μg/liter)				
Instrument	Micro Tek-H^3	Micro Tek-Ni^{63}	Aero-graph-H^3	Overall
Number of results	4	9	8	34
Number of outliers	2	0	0	5
Mean	1.12	1.25	1.39	1.25
Mean Error	0.12	0.25	0.39	0.25
Standard Deviation	0.07	0.39	0.42	0.44
Relative Error	11.8	25.0	39.0	24.7
Relative Standard Deviation	5.9	31.5	30.2	35.4

Table 21. SUMMARY OF RESULTS FOR ENDRIN IN SAMPLE 3

(0.10 µg/liter)				
Instrument	Micro Tek-H[3]	Micro Tek-Ni[63]	Aero-graph-H[3]	Overall
Number of results	4	9	8	31
Number of outliers	2	0	0	5
Mean	0.100	0.125	0.119	0.116
Mean Error	0.000	0.025	0.019	0.016
Standard Deviation	0.034	0.394	0.094	0.045
Relative Error	0.0	25.0	19.0	16.0
Relative Standard Deviation	33.6	31.5	79.3	38.8

COMMENTS OF THE PARTICIPANTS

1. Recovery factors.....were calculated using standards of the concentration indicated.

Lindane	25 µg/liter - 88% 0.1 µg/liter - 83%
Heptachlor	25 µg/liter - 84% 0.1 µg/liter - 86%
Heptachlor Epoxide	25 µg/liter - 94% 0.1 µg/liter - 97%
p,p'-DDT	25 µg/liter - 89% 0.1 µg/liter - 85%
Endrin	25 µg/liter - 99% 0.1 µg/liter - 95%

Recoveries were determined by taking.....the indicated quantities of pesticides through the complete extraction, clean-up and determination procedure.

2. Ran in pulse mode, 90% Ar-10% CH_4 carrier. All results obtained on 8% QF-1 + 2% OV-17, Gas Chrom Q.

3. The transfer of the hexane layer to a separatory funnel after extraction is no good. Recoveries are very low.

4. Column (5% SE-30 on Aeropack) did not separate endrin well enough for a proper determination.

5. .....using small (1/8") columns, I keep my injections in the range of 1 to 2 μl to minimize overloading.

6. Had poor extraction efficiency for heptachlor (0.527) and p,p'-DDT (0.381). Adding HCl or a salt or using a polar solvent such as ethyl ether mixed with hexane would help.

7. Checked recovery of aldrin only 99 percent, applied 90 percent recovery to everything (Editorial note: see comment 1).

8. Standing current varied from 22 to 38 percent depending upon detector cleanliness.

9. Endrin decomposed on column to three unidentifiable components.

10. Evaporation Concentrator - Flash evaporator substituted for Kuderna Danish (operated at 30°C and 26" Hg).

11. Heptachlor epoxide recovery assumed to be 70 percent. Unable to secure standard for recovery determination in time for submission of results.

12. Separations were attempted on the columns described in the method. Resolution was poor on 10% DC-200 and fair on the mixed column. According to general experience in our laboratories, the lower loaded columns give sharper separations of pesticides. N. B. Co. reference materials were used for standards. These are commercial products and the analysis statements appear to be only approximate.

SUMMARY AND CONCLUSIONS

In this study the participants were asked to analyze the samples by a recommended method, which prescribed specific techniques for the extraction and clean-up and suggested the parameters at which to operate the gas chromatograph in the determinative step of the analysis.

Two extraction techniques, the prescribed jug technique and the separatory funnel technique, were used. Also, many different gas chromatographic parameters were used. These include 27 different gas chromatographic columns; basically four kinds of detectors, the Ni^{63} parallel plate electron capture detector, the tritium concentric tube and parallel plate electron capture detectors, the non-radioactive electron capture detector and the microcoulometric detector; as well as various carrier flow rates, and many different compartment tempera-

atures. Thus, it was rather arbitrary to divide the data into groups according to the types of instrument (which dictated the size of column and type of detector) used in carrying out the analysis, for actually no two participants with the same instruments used exactly the same method. Each had some variable, namely, a different column packing, extraction technique, gas flow rate or column temperature, etc. Nevertheless, it is interesting to note that instrument 2 equipped with a Ni^{63} parallel plate detector and a 1/4" column, and instrument 3 equipped with a tritium concentric tube detector and a 1/8" column gave accurate and precise results more often than instrument 1. There were, however, some very good individual determinations using instrument 1, (tritium parallal plate detector with a 1/4" column).

Overall, regardless of instrument used, the accuracy of the data was generally acceptable (namely, the relative error was over 15 percent in only four cases out of eighteen. On the other hand the precision in general, was unacceptable, namely; in only one case was the relative standard deviation less than 20 percent.

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APPENDICES

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APPENDIX A

METHOD OF ANALYSIS FOR CHLORINATED HYDROCARBON PESTICIDES IN NATURAL AND TREATED WATERS IN THE ABSENCE OF GROSS POLLUTION

The increasing application of pesticides in large-scale agriculture and in forest areas can contribute to the presence of these toxic materials in a water supply. Contamination can occur through drainage from the surrounding terrain, precipitation from the atmosphere, accidental spills of pesticides in the watershed area, or a cross connection on a distribution system

Experimental investigations have demonstrated that conventional water treatment processes (in the absence of carbon) are capable of coping with DDT but are considerably less effective against most of the other chlorinated hydrocarbons.

1. GENERAL DISCUSSION

1.1. Principle: Gas chromatography is the most useful single technique presently available to the residue analyst. The mobile phase, called the carrier gas, is a permanent gas such as N_2, Ar, He, or H_2. The stationary phase is a liquid that has been impregnated on a granular support. This constitutes the column packing which is held in a glass or metal tubing. The column is installed in an oven so that the inlet is attached to a heated injector block and the outlet is attached to a detector. Precise and constant temperature control of the injector block, the oven and the detector is critical. Stationary phase material and concentration, column length and diameter, oven temperature, gas flow and detector type are controllable variables.

Minute volumes of the sample solution are injected through a rubber septum into the injector block using a micro syringe. The pesticides vaporize and are moved through the column by the carrier gas. They travel through the column at different rates depending on differences in their partition coefficients between the mobile and stationary phase. As each component of the sample passes through the detector, a quantitatively proportional electrical signal is sent to a stripchart recorder. Each component is observed as a peak on a continuous line. The elution time is indicative of the particular pesticide and the peak height is proportional to the quantity that was injected.

The manipulation of variables may be used to obtain important confirmatory identification data. For example, the detector system is somewhat optional depending on the specificity and sensitivity needed. The use of specific response detectors can supply valuable data. The detector used in this method is a tritium foil electron capture detector which is very sensitive to chlorinated compounds. Additional confirmatory identification can be made from retention data of two or more columns where the stationary phases are different polarities. This method describes a two column procedure that has been found particularly useful.

1.2. Interference: There are some substances besides chlorinated compounds that effect responses by the electron capture detector. Among these are oxygenated and unsaturated compounds. Sometimes plant or animal extractives essentially obscure the pesticide peaks. These interfering substances can often be removed by ancillary, "cleanup", techniques. This method describes a Florisil column cleanup.

1.3. Detection Limits: The ultimate detection limit of a substance is effected by a number of factors, e.g., the detector sensitivity, the extraction and cleanup efficiency, the concentrations, and attenuation setting at an acceptable chromatogram baseline noise level. Lindane can usually be determined at 0.01 μg/l in a sample of relatively unpolluted water; the DDT detection limit will be somewhat higher.

It should be noted that the higher the sensitivity desired, the more the interference, and the greater the number of pesticides investigated, the longer the time required for an analysis.

2. APPARATUS

2.1. Sample bottles* — 1 gallon, glass with teflon lined screw cap. Place permanent calibration mark 2 inches below the mouth of the bottle; measure and record the volume contained

2.2. Evaporative Concentrator* — Kuderna-Danish, 250 ml flask, and 10 ml graduated lower tube, or equivalent.

2.3. Separatory funnels* — 250 ml capacity.

*All glassware should be carefully washed with soap and water, rinsed with tap water then with distilled water and finally thoroughly rinsed at least three times with A. R. grade or better acetone. The glassware should be allowed to drain between rinsings. The glass wool should be thoroughly extracted with acetone or other suitable solvent and dried.

2.4. Erlenmeyer flasks* — 500 ml capacity, glass stoppered.

2.5. Chromatographic column* — 20 mm diameter X 400 mm length.

2.6. Miscellaneous glassware* — small funnels, glass wool, transfer pipets, miscellaneous volumetric flasks, assorted beakers, etc.

2.7. Magnetic stirrer — large, with 1 5/8" teflon coated bar.

2.8. Microsyringes — suitable for injecting 1 to 8 µl of solutions. (Hamilton 701-N or equivalent).

2.9. Steam bath — should be in a hood to vent solvent fumes.

2.10. Gas chromatograph system — There are many variations in gas chromatograph instrumentation. The operating procedures may vary accordingly. It is highly desirable for each chromatographer to be familiar with the manufacturer's operating manuals, gas chromatography catalogues, and other references (see bibliography).

a. Carrier gas line should have a molecular sieve drying cartridge. The carrier gas must be dry and there must be no gas leaks throughout the system.

b. Oven temperature must be very stable at the desired setting.

c. Chromatographic columns may be purchased, or prepared in the laboratory. It is not appropriate to rigidly specify the size or compositions to be used since experience has shown that some instruments perform better using different columns than do others. Good separations have been attained using 10% DC-200 on 80/90 mesh Anakrom ABS in a 1/4" o.d. by 6' long column. A good confirmatory column is 4% DC-200 and 6% QF-1 with the same support and dimensions. A column is suitable when it effects clean, reproducible separations.

To prepare a 10% DC-200 column, dissolve 2g DC-200 in 50 ml ethyl acetate in a 250 ml beaker. Slowly add 20g Anakrom ABS with stirring. Occasionally swirl to mix the solution and the support while evaporating the solvent on the steam bath. When the mixture becomes a thick slurry, gently spread it in a thin layer in a shallow dish and air dry. Drying is completed in an oven at 100°C for 2 hours and then the material is preconditioned at 230°C for 2 to 4 hours.

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*See footnote on page 23.

Select a tubing prefitted to the chromatograph oven, lightly pack a glass wool plug into one end, apply vacuum to that end and introduce the prepared packing into the other end. Tap or vibrate the tubing until it is firmly filled, then place a glass wool plug in the end.

Place the column in the normal operating position in the gas chromatograph. As soon as the temperature and gas flow have stabilized, the column is ready for use.

The second column is prepared in the same manner after dissolving 0.8 g DC-200 and 1.2 g QF-1 in 50 ml ethyl acetate.

Some tubing materials catalyze sample component decomposition within the column. The most inactive material is pyrex glass, but due to the breakage hazard, aluminum or some stainless steel tubings may be preferred. Do not use copper.

d. Detector, electron capture with DC power supply.

e. Strip chart recorder must be compatible with the electrometer.

f. Operating parameters should be kept as simple and reproducible as possible. Conditions that have produced satisfactory chromatograms for pesticide analyses are:

Injector temperature - 230° C

Oven temperature - 180° C

Detector temperature - 200° C

Carrier gas flow rate - 120 ml/min

Electrometer, input and output attenuations, Detector voltage supply, Recorder gain and damping - adjust in accordance with operating manual for optimum sensitivity and linearity.

3. REAGENTS

3.1. Hexane*

3.2. Petroleum ether*

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*See footnote on page 26.

3.3. Diethyl ether*

3.4. Ethyl acetate*

3.5. Mixed ethers - mix one volume diethyl ether with three volumes redistilled petroleum ether.

3.6. Florisil* — activated at 650° C and stored at 130° C.

3.7. Sodium sulfate* — anhydrous granular.

3.8. Anakrom ABS — 80/90 mesh or equivalent.

3.9. DC-200 Silicone fluid — 12,500 centistokes.

3.10. QF-1 Fluorosilicone

3.11. Nitrogen gas — purified grade, should be moisture and O_2 free.

3.12. Pesticide concentrates — pure substances when possible. These may be obtained from chromatographic equipment suppliers.

3.13. Stock pesticide solutions — 1.0 mg per ml, dissolve 100 mg of the pesticides of interest in ethyl acetate and dilute to 100 ml in a volumetric flask.

3.14. Intermediate standard solutions — 10 µg/ml, dilute 1.0 ml stock pesticides solution to 100 ml with ethyl acetate.

3.15. Working standard solutions — final concentration is dependent on the detector sensitivity and linearity. Normally, a concentration that would cause a peak height of about 10 chart-percent when 1 µl is injected is suitable. If 20 pg (picogram) of lindane will cause a 10 chart-percent deflection, the working standard solution can be prepared at 20 pg/µl by diluting 0.2 ml of the intermediate standard solution to 100 ml with hexane.

Mixtures of pesticides can be prepared and conveniently used; however, mixtures of pesticides that have very similar retention times should be avoided.

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*All reagents are to be free of interfering peaks when used as in the procedure. Laboratory distillation of solvents in glass can be suitable, but it is usually easier and cheaper to purchase chromatographic grade solvents.

4. PROCEDURE

4.1. Sample Collection: Fill the bottle to the calibration mark only.

4.2. Extraction of Pesticides: Insert a magnetic stirring bar, add 10 ml of hexane to the sample, and loosely screw on the cap. Place the bottle on the magnetic stirrer somewhat off center in order to cause greater displacement and circulation of the hexane in the form of small drops in the water. Stir the sample fast enough to cause dispersion of the hexane through the sample, but no faster than necessary. After 15 minutes allow the phases to separate. Remove the hexane layer to a small separatory funnel using a transfer pipet. Since it is impossible to remove all the hexane, add a small amount of hexane to the residual solution and again remove this to the separatory funnel. Repeat this step once more, thus minimizing the pesticide left in the sample bottle. Add 10 ml hexane and repeat the extraction procedure combining the extracts in the separatory funnel.

Separate the water from the hexane and then dry the hexane by transferring* to an erlenmeyer flask containing about 10 grams of anhydrous sodium sulfate. Transfer the dried solution to an evaporative concentrator (Kuderna-Danish or equivalent) and reduce the volume to about 7 ml. Quantitatively transfer the solution to a 10 ml volumetric flask and dilute to volume.

4.3. Chromatography: Five μl** of the extract solution is injected into one of the columns of the gas chromatograph. The resulting chromatogram is inspected for peaks corresponding to the pesticides of concern. It is also evaluated for the presence of significant interference. It is desirable at this point to determine whether the sensitivity is adequate.

a. If there are presumptive pesticide peaks and no significant interference, then rechromatograph 5.0 μl of the extract solution over the alternate column. See Section 5 for the next step.

b. The extract solution may be concentrated for greater sensitivity or diluted when a peak is too large. Similar effects can be attained by adjustment of the electrometer attenuator.

c. If significant interference is present it is necessary to use a cleanup procedure. See Section 4.4.

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*All hexane transfers are to be done quantitatively with several rinsings of small amounts of fresh hexane.

**It is desirable to always inject the same amount of liquid.

4.4. Cleanup: Several cleanup procedures have been devised. Their purpose is to separate the interfering substances from the pesticide materials in the extract. Some of the techniques effect a preliminary separation of the pesticides which can simplify interpretation of the chromatogram. In this method, only one cleanup method is given; a Florisil column technique.

A 20 mm by 4 inch Florisil column is compacted by vibrating or tapping and a one inch layer of sodium sulfate is added. The column is wetted by the addition of 40 ml of petroleum ether. The eluate is discarded. When the liquid surface reaches the column surface, a selected portion of the extract solution is added to the column. The eluate is collected. When the liquid surface reaches the column surface, 200 ml of the mixed ether reagent is added and the eluate collected. The solvents are evaporated as outlined in Section 4.2 and diluted to appropriate volume.

5. QUANTITATION

5.1. Standard Curves: Inject a series of increasing amounts of a pesticide into one of the columns. Injections of 1 μl to 5 μl may be used if the 1 μl volume is backed up with 4 μl of solvent, etc. More than one concentration may be needed to extend the series. Measure each peak height from base line and plot the quantity of pesticide vs. peak height. Mixed solutions may be used as long as the peaks do not mutually interfere.

5.2. Extraction Efficiency: Add known amounts of pesticides in ethyl acetate solution to three and three-fourths liters of water and carry through the same procedure as the samples. Dilute an equal amount of the intermediate standard to the same final volume. Call the peak height from the standard "a", and the peak height from the spiked sample "b". The Efficiency (E) = $\frac{b}{a}$. The extraction efficiency and a control blank should be determined periodically by each chromatographer to test the procedure.

5.3. Dilution factor: If the portion of the extract solution was concentrated, the dilution factor (C) is a decimal. If it was diluted, the dilution factor is greater than 1.

5.4. Attenuation factor: Each upward step of the attenuator switch has the same effect as diluting the sample solution. The chromatographer must determine that the linear sample response range is not exceeded when attenuation is used. Attenuation factor (G) = dial setting for the sample peak divided by dial setting for the standard peak.

5.5. Units: The sensitivity of the gas chromatograph is such that the units of mass and volume extend below those normally encountered. Thus 1 ml = 10^3 µl (Micro liters); [1 mg = 10^3 µg = 10^6 ng (nanograms) = 10^9 pg (picograms)].

Note that in these units, water density is 1 mg/µl.

5.6. Calculations:

$$\frac{\text{wt. of pesticide}}{\text{liter}} = \frac{A \times C \times F \times G}{B \times D \times E}$$

A = nanograms of pesticide injected into chromatograph (interpolated from the standard curve).

B = volume of solution injected (µl).

C = volume of extract solution (expressed in µl).

D = sample volume in liters.

E = extraction efficiency.

F = dilution factor.

G = attenuation factor.

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APPENDIX B

TABULATION OF RESULTS

Table B-1. TABULATION OF RESULTS FOR LINDANE

Sample 1, 25.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	22.00	8	6552	25.00	5
1124	28.00	3	6715	29.20	4
1524	4.60	1	6911	4.54	1
2211	3.00	5	7112	27.00	3
2311	15.42	1	7123	7.11	4
2811	19.54	7	7424	19.50	2
3111	18.52	1	7622	21.57	3
3351	49.00	4	7813	21.86	3
3411	27.20	1	7813	19.70	3
3511	49.00	2	7813	21.16	9
3611	6.53	6	7911	27.50	2
4112	3.30	7	7914	19.50	3
4511	25.30	2	8211	23.05	2
4515	24.60	5	8251	17.90	3
4611	13.75	1	8322	10.28	3
4811	32.90	3	9111	19.10	2
5136	25.25	2	9123	19.81	7
5351	19.33	3	9613	14.20	1
6411	20.00	6			

(Table B-1 continued)

Sample 2, 5.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	5.70	8	6411	3.00	6
1124	5.70	3	6552	4.10	5
1524	1.58	1	6715	5.55	4
2211	0.35	5	6911	1.04	1
2311	2.97	1	7112	5.50	3
2513	4.87	2	7123	2.40	4
2811	3.89	7	7424	3.64	2
3111	4.90	1	7622	3.24	3
3351	5.00	4	7813	5.17	3
3411	5.42	1	7813	5.00	3
3511	8.60	2	7813	4.70	9
3611	1.40	6	7911	7.00	2
4112	1.50	7	7914	8.30	3
4511	5.05	2	8211	4.94	2
4515	5.11	5	8251	4.84	3
4611	2.65	1	8322	2.30	3
4811	5.32	3	9111	4.20	2
5136	5.48	2	9123	4.77	7
5351	3.73	3	9613	6.20	1

(Table B-1 continued)

Sample 3, 0.50 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	0.55	8	6411	0.24	6
1124	0.52	3	6552	0.40	5
1524	0.24	1	6715	5.24	4
2211	0.10	5	6911	0.24	1
2311	0.30	1	7112	0.45	3
2513	0.77	2	7123	0.27	4
2811	0.40	7	7424	0.36	2
3111	0.48	1	7622	0.26	3
3351	0.50	4	7813	0.45	3
3411	0.48	1	7813	0.50	3
3511	0.70	2	7813	0.36	9
3611	0.27	6	7911	0.69	2
4112	0.34	7	7914	1.98	3
4511	0.50	2	8211	0.48	2
4515	0.52	5	8251	0.45	3
4611	0.25	1	8322	0.71	3
4811	0.59	3	9111	0.36	2
5136	0.47	2	9123	0.45	7
5351	0.24	3	9613	0.34	1

Table B-2. TABULATION OF RESULTS FOR HEPTACHLOR

Sample 1, 15.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	15.50	8	6552	15.00	5
1124	16.00	3	6715	26.70	4
1524	5.50	2	6911	5.96	1
2211	0.00	5	7112	17.00	3
2311	6.42	1	7123	12.89	4
2811	24.61	7	7424	10.80	2
3111	8.92	1	7622	12.16	3
3351	15.60	4	7813	14.49	3
3411	11.56	1	7813	19.40	3
3511	12.00	2	7813	15.57	9
3611	8.16	6	7911	15.45	2
4112	4.70	7	7914	16.00	3
4511	13.27	2	8211	17.50	2
4515	14.20	5	8251	13.80	3
4611	17.50	1	8322	5.85	3
4811	18.10	3	9111	10.90	2
5136	11.43	2	9123	14.42	7
5351	14.67	3	9613	17.50	1
6411	6.75	6			

(Table B-2 continued)

Sample 2, 7.50 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	8.10	8	6411	3.00	6
1124	8.30	3	6552	5.50	5
1524	2.40	2	6715	14.17	4
2211	0.50	5	6911	1.77	1
2311	3.37	1	7112	7.00	3
2513	6.38	2	7123	5.44	4
2811	11.23	7	7424	5.57	2
3111	3.85	1	7622	5.12	3
3351	5.80	4	7813	7.11	3
3411	5.75	1	7813	6.82	3
3511	6.20	2	7813	7.86	9
3611	7.42	6	7911	8.36	2
4112	1.70	7	7914	16.30	3
4511	7.55	2	8211	9.57	2
4515	7.41	5	8251	5.79	3
4611	10.00	1	8322	1.35	3
4811	6.71	3	9111	6.70	2
5136	4.63	2	9123	7.70	7
5351	6.23	3	9613	9.10	1

(Table B-2 continued)

Sample 3, 1.00 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	1.05	8	6411	0.38	6
1124	1.02	3	6552	0.35	5
1524	0.47	2	6715	1.66	4
2211	0.20	5	6911	0.45	1
2311	0.46	1	7112	1.10	3
2513	0.99	2	7123	0.63	4
2811	1.45	7	7424	0.75	2
3111	0.65	1	7622	0.83	3
3351	0.96	4	7813	1.03	3
3411	0.51	1	7813	1.16	3
3511	0.80	2	7813	0.88	9
3611	0.75	6	7911	1.11	2
4112	0.49	7	7914	2.25	3
4511	0.94	2	8211	1.25	2
4515	1.01	5	8251	0.78	3
4611	1.00	1	8322	1.19	3
4811	1.14	3	9111	0.76	2
5136	1.18	2	9123	1.00	7
5351	0.30	3	9613	1.10	1

Table B-3. TABULATION OF RESULTS FOR HEPTACHLOR EPOXIDE

Sample 1, 15.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	15.70	8	6552	20.00	5
1124	20.00	3	6715	16.30	4
1524	6.20	2	6911	8.01	1
2211	0.80	5	7112	17.00	3
2311	12.60	1	7123	11.29	4
2811	22.00	7	7424	10.00	2
3111	14.50	1	7622	12.53	3
3351	15.80	4	7813	15.08	3
3411	12.47	1	7813	15.89	3
3511	23.50	2	7813	14.88	9
3611	11.00	6	7911	17.15	2
4112	16.40	7	7914	17.00	3
4511	14.57	2	8211	15.05	2
4515	14.00	5	8251	14.00	3
4611	18.75	1	8322	10.09	3
4811	17.80	3	9111	12.70	2
5136	12.62	2	9123	15.10	7
5351	14.98	3	9613	12.70	1
6411	9.00	6			

(Table B-3 continued)

Sample 2, 7.50 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	8.10	8	6411	4.70	6
1124	8.70	3	6552	6.50	5
1524	2.80	2	6715	8.03	4
2211	0.25	5	6911	2.59	1
2311	6.50	1	7112	9.70	3
2513	7.79	2	7123	4.94	4
2811	9.50	7	7424	5.57	2
3111	7.09	1	7622	5.36	3
3351	5.80	4	7813	7.59	3
3411	6.33	1	7813	7.36	3
3511	12.10	2	7813	7.14	9
3611	10.73	6	7911	9.66	2
4112	6.80	7	7914	8.50	3
4511	7.62	2	8211	7.97	2
4515	7.43	5	8251	6.25	3
4611	9.50	1	8322	5.42	3
4811	6.81	3	9111	6.70	2
5136	7.70	2	9123	7.67	7
5351	4.90	3	9613	7.50	1

(Table B-3 continued)

Sample 3, 1.00 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	1.09	8	6411	0.60	6
1124	1.02	3	6552	0.75	5
1524	0.41	2	6715	1.05	4
2211	0.10	5	6911	0.61	1
2311	0.84	1	7112	1.10	3
2513	1.02	2	7123	0.65	4
2811	1.23	7	7424	0.70	2
3111	0.99	1	7622	0.78	3
3351	1.00	4	7813	1.11	3
3411	0.73	1	7813	1.22	3
3511	1.30	2	7813	0.76	9
3611	0.90	6	7911	1.28	2
4112	1.90	7	7914	1.93	3
4511	0.97	2	8211	1.05	2
4515	0.97	5	8251	0.84	3
4611	1.00	1	8322	0.77	3
4811	1.03	3	9111	0.79	2
5136	0.70	2	9123	0.96	7
5351	0.34	3	9613	0.90	1

Table B-4. TABULATION OF RESULTS FOR DIELDRIN

Sample 1, 15.00 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	16.50	8	6552	20.09	5
1124	21.00	3	6715	15.50	4
1524	3.40	1	6911	8.86	1
2211	1.60	5	7112	17.00	3
2311	10.46	1	7123	10.38	4
2811	23.98	7	7424	10.80	2
3111	12.68	1	7622	9.36	3
3351	15.00	4	7813	13.74	3
3411	12.75	1	7813	13.77	3
3511	15.80	2	7813	13.92	9
3611	10.58	6	7911	20.94	2
4112	5.30	7	7914	35.00	3
4511	12.72	2	8211	14.45	2
4515	13.70	5	8251	14.60	3
4611	16.25	1	8322	13.23	3
4811	15.10	3	9111	10.20	2
5136	23.65	2	9123	14.03	7
5351	14.26	3	9613	14.05	1
6411	8.00	6			

(Table B-4 continued)

Sample 2, 5.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	6.00	8	6411	2.30	6
1124	6.20	3	6552	6.00	5
1524	1.46	1	6715	5.50	4
2311	0.50	5	6911	2.70	1
2311	3.56	1	7112	6.00	3
2513	5.56	2	7123	3.60	4
2811	8.13	7	7424	3.64	2
3111	4.40	1	7622	5.38	3
3351	4.50	4	7813	4.74	3
3411	4.25	1	7813	5.21	3
3511	5.10	2	7813	3.82	9
3611	2.32	6	7911	7.85	2
4112	2.00	7	7914	14.00	3
4511	4.96	2	8211	5.50	2
4515	4.66	5	8251	4.54	3
4611	6.50	1	8322	5.29	3
4811	4.50	3	9111	3.20	2
5136	8.75	2	9123	4.91	7
5351	3.32	3	9613	7.65	1

(Table B-4 continued)

Sample 3, 0.25 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	0.31	8	6411	0.13	6
1124	0.29	3	6552	0.15	5
1524	0.06	1	6715	0.24	4
2211	0.05	5	6911	0.26	1
2311	0.18	1	7112	0.18	3
2513	0.31	2	7123	0.24	4
2811	0.61	7	7424	2.10	2
3111	0.27	1	7622	0.25	3
3351	0.21	4	7813	0.23	3
3411	0.17	1	7813	0.25	3
3511	0.20	2	7815	0.21	9
3611	0.54	6	7911	0.42	2
4112	0.22	7	7914	0.83	3
4511	0.22	2	8211	0.24	2
4515	0.26	5	8251	0.16	3
4611	0.45	1	8322	0.34	3
4811	0.16	3	9111	0.16	2
5136	2.65	2	9123	0.28	7
5351	0.06	3	9613	0.38	1

Table B-5. TABULATION OF RESULTS FOR p, p'-DDT

Sample 1, 20.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	20.80	8	6552	25.00	5
1124	24.00	3	6715	52.50	4
1524	10.00	1	6911	12.10	1
2211	2.00	5	7112	21.00	3
2311	17.52	1	7123	19.32	4
2811	56.01	7	7424	23.70	2
3111	23.61	1	7622	23.90	3
3351	19.00	4	7813	21.11	3
3411	16.30	1	7813	21.68	3
3511	23.20	2	7813	17.24	9
3611	9.30	6	7911	21.20	2
4112	15.00	7	7914	38.00	3
4511	20.10	2	8211	20.25	2
4515	19.70	5	8251	17.00	3
4611	22.50	1	8322	13.14	3
4811	19.70	3	9111	19.20	2
5136	4.73	2	9123	19.57	7
5351	31.14	3	9613	25.05	1
6411	11.00	6			

(Table B-5 continued)

Sample 2, 5.00 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	5.30	8	6411	3.35	6
1124	5.20	3	6552	15.00	5
1524	2.60	1	6715	13.29	4
2211	0.25	5	6911	3.20	1
2311	4.75	1	7112	4.90	3
2513	10.00	2	7123	5.17	4
2811	18.74	7	7424	5.83	2
3111	4.88	1	7622	4.84	3
3351	4.40	4	7813	5.72	3
3411	3.54	1	7813	5.53	3
3511	6.30	2	7813	3.72	9
3611	11.80	6	7911	6.75	2
4112	3.00	7	7914	5.75	3
4511	4.76	2	8211	5.69	2
4515	5.47	5	8251	5.85	3
4611	7.00	1	8322	4.53	3
4811	6.03	3	9111	4.80	2
5136	2.25	2	9123	4.86	7
5351	5.52	3	9613	8.80	1

(Table B-5 continued)

Sample 3, 0.50 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	0.50	8	6411	0.30	6
1124	0.48	3	6552	0.20	5
1524	0.49	1	6715	1.17	4
2211	0.05	5	6911	0.42	1
2311	0.45	1	7112	0.43	3
2513	0.65	2	7123	0.59	4
2811	2.38	7	7424	0.67	2
3111	0.56	1	7622	0.75	3
3351	0.39	4	7813	0.52	3
3411	0.09	1	7813	0.54	3
3511	0.70	2	7813	0.28	9
3611	0.33	6	7911	0.66	2
4112	0.19	7	7914	0.70	3
4511	0.47	2	8211	0.52	2
4515	0.56	5	8251	0.42	3
4611	0.85	1	8322	0.43	3
4811	0.54	3	9111	0.39	2
5136	0.42	2	9123	0.45	7
5351	0.32	3	9613	0.70	1

Table B-6. TABULATION OF RESULTS FOR ENDRIN

Sample 1, 10.00 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	13.70	8	6411	8.00	6
1124	14.00	3	6552	12.50	5
1524	5.40	1	6715	11.91	4
2211	2.00	5	6911	8.02	1
2311	9.98	1	7112	12.00	3
2811	20.98	7	7123	10.08	4
3111	9.57	1	7424	9.30	2
3351	11.20	4	7622	9.78	3
3411	9.40	1	7813	9.95	3
3511	11.60	2	7813	10.09	9
3611	7.90	6	7911	12.40	2
4112	5.20	7	7914	19.50	3
4511	8.77	2	8211	11.15	2
4515	10.80	5	8251	12.30	3
4611	10.00	1	8322	9.45	3
4811	11.50	3	9111	11.10	2
5136	13.78	2	9123	9.98	7
5351	10.65	3	9613	15.40	1

(Table B-6 continued)

Sample 2, 1.00 μg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	1.50	8	6411	0.60	6
1124	1.50	3	6552	1.50	5
1524	1.02	1	6715	1.38	4
2211	0.25	5	6911	1.12	1
2311	1.04	1	7112	2.00	3
2513	1.57	2	7123	1.02	4
2811	0.00	7	7424	1.08	2
3111	1.20	1	7622	1.84	3
3351	1.20	4	7813	1.17	3
3411	1.11	1	7813	0.74	9
3511	1.70	2	7911	1.00	2
3611	5.23	6	7914	1.15	3
4112	0.76	7	8211	1.27	2
4511	0.54	2	8251	1.23	3
4515	1.21	5	8322	1.55	3
4611	2.00	1	9111	1.30	2
5136	1.80	2	9123	1.10	7
5351	0.69	3	9613	2.25	1

(Table B-6 continued)

Sample 3, 0.10 µg/liter					
LAB. NO.	RESULTS	METHOD	LAB. NO.	RESULTS	METHOD
0003	0.17	8	6552	0.10	5
1124	0.15	3	6715	0.11	4
1524	0.05	1	6911	0.14	1
2311	0.06	1	7112	0.16	3
2513	0.06	2	7123	0.10	4
2811	0.50	7	7424	0.14	2
3111	0.09	1	7622	0.13	3
3351	0.08	4	7813	0.11	3
3411	0.28	1	7813	0.07	9
3511	0.10	2	7911	0.11	2
3611	0.02	6	7914	0.14	3
4112	0.11	7	8211	0.10	2
4511	0.10	2	8251	0.10	3
4515	0.12	5	8322	0.10	3
4611	0.11	1	9111	0.51	2
5136	1.39	2	9123	0.11	7
5351	0.06	3	9613	0.21	1
6411	0.10	6			

APPENDIX C

CALCULATION OF COLUMN EFFICIENCY

Efficiency values were calculated using the equation:

$$N = 16 \left(\frac{x}{y}\right)^2$$

where N = total theoretical plates

X = distance in mm from injection point to peak center

Y = width of peak base in mm

and the equation:

$$HETP = L/N$$

where HETP = the average height equivalent to a theoretical plate

L = length of the column in centimeters

N = total theoretical plates

APPENDIX D

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniformity of understanding.

Arithmetic mean — The sum of the sample results divided by the number of results in the sample. Let X_i ($i = 1, 2, \ldots n$) denote the i^{th} results in a sample of n results. The arithmetic mean denoted $\overline{X}$ is given by $\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$.

Median — Halfway point in the results when they have been arranged in order of magnitude (the middle result of an odd number of results, or the average of the middle two for an even number).

Accuracy — The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).

Measures of accuracy — Measures that relate to the difference between the mean of the results and the true value when the latter is known or assumed. The following measures apply:

Mean error — The average difference with regard to sign between the results and the true value. Equivalently, the difference between the mean of the results and the true value (T. V.).

$$\text{Mean error} = \overline{X} - \text{T. V.}$$

Relative error — The absolute value of the mean error expressed as a percentage of the true value.

$$\text{Relative error} = \frac{|\overline{X} - \text{T. V.}|}{\text{T. V.}} \times 100$$

Precision — The reproducibility of sample results or the degree of agreement among the results.

Measures of precision

Measures of the variation among the sample results themselves, i.e., the spread or dispersion of the results without regard to the true value. The following measures apply:

Sample variance — Sum of squared deviations of the sample results from their mean divided by one less than the number of results in the sample. The sample variance denoted s^2 is given by

$$s^2 = \frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}$$

where n is the number of results.

Sample standard deviation — Square root of the sample variance.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{n - 1}}$$

Relative standard deviation (coefficient of variation) — Sample standard deviation expressed as a percentage of the mean.

$$\text{Rel. Std. Dev.} = \frac{s}{\overline{X}} \times 100$$

Range — The difference between the largest and smallest results in the sample

Confidence limits — Limits within which the true mean, μ, of the population (the theoretically infinite number of possible replications of the analysis) will lie with probability equal to $1 - \alpha$, where α is the probability that the limits do not contain the true mean. The upper and lower $1 - \alpha$ confidence limits are given by

$$\text{Confidence limits} = \overline{X} \pm t_{\alpha/2} s/\sqrt{n}$$

where $\overline{X}$ and s are the sample mean and standard deviation, $t_{\alpha/2}$ is the upper $\alpha/2$ point of "Student's" t-distribution, and n is the number of results in the sample used to compute $\overline{X}$.

Tolerance limits – Limits within which one can state with probability γ that at least a proportion P of the entire population will lie. The upper and lower tolerance limits are given by

$$\text{Tolerance limits} = \overline{X} \pm Ks,$$

where K is the factor for two-sided tolerance limits for normal populations.[1] The value of K depends upon the chosen values of γ and P.

REFERENCES

1. Natrella, M. G. Experimental Statistics. National Bureau of Standards, 1963, pp. T-10.

APPENDIX E

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness-of-fit test was used to determine whether the observations reported could reasonably be thought to have come from a normal distribution.[1]

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it with the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness-of-fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations; otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon.[2] Briefly, this test involves computing a ratio that compares the distance of the suspected value being tested from its neighbors with the range of all, or most all, of the observations (depending on the total number of suspected values in the sample). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability that the suspected outlier is from the sample distribution is small; hence, the outlier is rejected. If the ratio is less than the critical value, the suspected outlier probably came from the sample distribution; hence, the suspected outlier is accepted.

3. If the distribution is designated as normal, and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[3] This method employs the statistic, $\frac{\overline{X} - X_o}{s}$, where $\overline{X}$ is the sample mean, X_o is the suspected outlier (the

farthest value from the mean) and s is the sample standard deviation. This statistic is compared with a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of tests for normality and for rejection of outliers to ARS studies

The test for normality and the subsequent test for rejection of outliers are applied to the observed data in two way: first, to each method for a given substance at a given concentration; then to a given substance at a given concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used to test for rejection of the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made, and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1. This cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal or a new distribution that was originally nonnormal is designated as normal after the rejection of one or more outliers, and if the number of observations is not greater than 30, then method 2 is used to test for rejection the suspected outlier farthest from the mean. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution is tested for rejection, and so on until the suspected value of a new distribution is not rejected; when this occurs, no further tests are made, and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made, and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of

observations is no longer greater than 30, in which case, method 2 is used for testing for rejection of any remaining suspected outliers.

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APPENDIX F

COMPARISON OF METHODS FOR STATISTICALLY SIGNIFICANT DIFFERENCES IN PRECISION AND ACCURACY

The methods are compared in two ways with respect to precision and accuracy. In the first case, two methods are compared at a given concentration with respect to precision and to accuracy. The unknown variances, σ_1^2 and σ_1^2 (estimated by the sample variances, s_1^2 and s_2^2), of the two methods are first compared by the F-test[1] to determine whether there is a significant difference in the precision of the two methods. The unknown means, μ_1 and μ_2 (estimated by the sample means, $\overline{X}_1$ and $\overline{X}_2$), of the two methods are then compared by the t-test[2] to determine whether there is a significant difference in the accuracy of the two methods. The t-test employed is based on the result of the F-test. These two tests of hypotheses will produce one of the following results.

$$\text{Outcome 1: } \sigma_1^2 = \sigma_2^2,\ \mu_1 = \mu_2$$

$$\text{Outcome 2: } \sigma_1^2 = \sigma_2^2,\ \mu_1 \neq \mu_2$$

$$\text{Outcome 3: } \sigma_1^2 \neq \sigma_2^2,\ \mu_1 = \mu_2$$

$$\text{Outcome 4: } \sigma_1^2 \neq \sigma_2^2,\ \mu_1 \neq \mu_2$$

In outcome 1, we conclude that the sample results do not indicate that a significant difference in either precision or accuracy exists between the two methods.

In outcome 2, we conclude that there is no indication of a significant difference in precision between the two methods, but there is a significant difference in the accuracy of the two methods; specifically, the method whose sample mean is closer to the true value is deemed the more accurate. In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the two methods, but the method with the smaller sample variance is the more precise.

In outcome 4, we conclude that there is a significant difference in the precision and in the accuracy of the two methods. The method with the smaller sample variance is the more precise, and the method whose sample mean is closer to the true value is the more accurate.

In the second case, more than two methods are compared at a given level of concentration with respect to precision and accuracy. Bartlett's

Test[3] is used first to test the hypothesis of equality of the unknown variances, σ_i^2, of the methods in order to compare the precision of the methods. If we conclude that the precision is the same, the Analysis of Variance[4] is then used to test whether a significant difference exists among the means, μ_i, in order to compare the accuracy of the methods. If there is a significant difference among the means. Duncan's Multiple Range Test [5, 6] is used to determine which method means differ significantly. If the precision is not the same, then the Kruskal-Wallis One-way Analysis of Variance by Ranks[7] is used to determine whether a significant difference exists among the means in order to compare the accuracy of the methods.

Once again, there are basically four possible outcomes for the above tests of hypotheses.

Outcome 1: all σ_i^2 are equal, all μ_i are equal

Outcome 2: all σ_i^2 are equal, not all μ_i are equal

Outcome 3: not all σ_i^2 are equal, all μ_i are equal

Outcome 4: not all σ_i^2 are equal, not all μ_i are equal

In outcome 1, we conclude that the sample results do not indicate a significant difference in either the precision or the accuracy of the methods.

In outcome 2, we conclude that there is no indication of a significant difference in the precision of the methods; however, at least one method does differ significantly from the rest with respect to accuracy, and Duncan's Multiple Range Test indicates which methods differ. For example, in comparing four methods, we might conclude $\mu_1 = \mu_2$ and $\mu_3 = \mu_4$, but μ_1 and μ_2 differ significantly from μ_3 and μ_4; or we might conclude that $\mu_1 = \mu_2 = \mu_3$, but μ_4 differs significantly from μ_1, μ_2, and μ_3.

In outcome 3, we conclude that there is no indication of a significant difference in the accuracy of the methods, but at least one method differs significantly from the rest with respect to precision.

In outcome 4, we conclude that the methods differ significantly with respect to both precision and accuracy.

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APPENDIX G

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California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation Laboratory, Berkeley
Colorado Department of Public Health, Denver
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Delaware Water and Air Resources Commission, Dover
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Florida State Board of Health, Jacksonville
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New York State Conservation Department, Ronkonkoma
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New York State Department of Health, Division of Laboratories and Research, Albany
New York State Department of Health, Syracuse
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